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# Modelling accelerated degradation test and shelf-life prediction of dye-sensitized solar cells with different types of solvents

Yu-Hsiang Wang, David Shan-Hill Wong *

*Department of Chemical Engineering, National Tsing Hua University, No. 101, Section 2, Guang Fu Road, Hsinchu 30013, Taiwan, Republic of China*

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## Abstract

Reliability of dye-sensitized solar cells has usually been reported by efficiency measurements after 1000 h at a certain elevated temperature. In this work, a protocol for shelf-life estimating was proposed. Accelerated degradation tests were performed at several elevated temperatures. The results were analyzed using the degradation model for the log ratio of efficiencies at different times to the initial efficiency. The model includes a linear degradation rate which may vary from unit-to-unit due to common-cause variations in assembly, and a Wiener stochastic process which account for random-walk effects between measurements. An Arrhenius-type acceleration factor was used to describe effects of temperature, which allows us to extrapolate and predict degradation cells efficiency at an ambient temperature. The procedure was demonstrated using three types of dye-sensitized solar cells: one using a volatile organic solvent 3-methoxy-propionitrile, one using a nonvolatile organic solvent polyethylene-glycol-dimethyl-ether, and one using an ionic liquid 1-ethyl-3-methyl-imidazolium tetra-cyanoborate. Use of ionic liquid not only reduces the mean degradation rate but also the unit-to-unit variations. If a residual efficiency limit of 80% was used, the mean shelf-life of cells using ionic liquid was predicted to be about 18,800 h, with 99.7% confidence limit that it is greater than 5900 h.

*Keywords:* Dye-sensitized solar cells; Accelerated degradation test; Shelf-life prediction

## 1. Introduction

Solar energy is a renewable and clean energy source. The sun supplies about $3 \times 10^{24}$J to the Earth per year, and converting 0.1% of this energy with solar cells (with an 10% efficiency) would satisfy our currently global needs (Gratzel, 2001). Dye-sensitized solar cells (DSSCs) have attracted much attention because of its low cost of materials and manufacture equipment, and the high photon-to-current conversion efficiency (Gratzel, 2003; Jena et al., 2012; Giribabu et al., 2012). A typical DSSC consist of a metal oxides film on transparent conductive oxide (TCO) glass as the anode, cathode are most commonly made of platinum (Pt) deposited on TCO, and an electrolyte system containing iodide/tri-iodide ($I^-/I^{3-}$) redox couple. The electrolyte is an important component and its properties have much effect on the conversion efficiency and stability of DSSCs. Outstanding conversion efficiencies exceeding 11% have been obtained using liquid electrolytes based on organic solvents such as acetonitrile (Gao et al., 2008). However, the high volatility of the solvent presents a great challenge to long-term reliability and practical use of DSSCs.

In order to improve the stability of DSSCs, extensive efforts have been focused on the search for stable electrolytes. Solidifying the electrolyte is a kind of method

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* Corresponding author. Tel.: +886 3 5721694.
*E-mail address:* dshwong@che.nthu.edu.tw (D.S.-H. Wong).

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to improve the stability of DSSCs. DSSCs filled with the quasi-solid-state (Kubo et al., 2002) or solid-state (Yang et al., 2006) electrolytes exhibited an excellent stability, the efficiency practically did not decrease at elevated temperature of 60 °C or 80 °C either under continuous light soaking or darkness. Using the room-temperature ionic liquids (RTILs) Wang et al., 2004, 2005; Kuang et al., 2006; Bai et al., 2008 such as 1-propyl-3-methyl-imidazolium iodide (PMII) or 1,3-dimethyl-imidazolium iodide (DMII) can also enhance the stability of DSSCs. The efficiency of DSSCs filled with RTILs kept about 90% of its initial value after 700 or 1000 h at elevated temperature tests. Using the organic sensitizers (Kuang et al., 2011; Feng et al., 2013), which are environmental friendly, easily to synthesize and cheap, are also a way to obtain high conversion efficiency and good long-term stability simultaneously.

As can be seen from the aforementioned literature, most of the stability tests have been conducted at elevated temperature of 60 °C or 80 °C either under continuous light soaking or darkness. Little quantitative conclusions about the shelf-life and the long term reliability of the product can be drawn. Products with different recipes that show good performance in the 1000-h test cannot be compared rigorously. Furthermore, the sources of degradation and variations cannot be identified.

High quality products are currently designed and manufactured to function for a long time before failures occur. To evaluate the reliability of the product, degradation data at different levels of accelerating stresses can be collected to construct an accelerated degradation model. The model can be used to extrapolate the life of the product at a certain stress level that corresponds to normal shelf-life. Such an experiment is called an accelerated degradation test (ADT). Nelson (1992) and Meeker and Escobar (2014) reviewed the degradation literature, surveyed their applications and described basic ideas on accelerated test degradation models.

A typical degradation model consists of a mean degradation path and different sources of variations. The mean degradation path is the characteristic of the degradation mechanism. The sources of variations include measurement errors, unit-to-unit variations caused by manufacturing process, or other stochastic effects during the test procedure. Measurement error and unit-to-unit variations are usually modeled by Gaussian process. The stochastic effects describe the correlation between successive measurements during the ADT and usually followed either a Wiener process (Hoel et al., 1972) or Gamma process.

For different products, different combinations of degradation path and sources of variation can be found. For example, Bae and Kvam (2004) presents a model for the emitted light level of vacuum fluorescent displays. A non-monotonic degradation path and unit-to-unit variations were considered. Park and Bae (2010) studied reliability of luminosity of the commercial organic light-emitting diode. A bi-exponential degradation path, unit-to-unit variations, and measurements errors were considered in the model. Yu and Tseng (2002) and Tseng and Peng (2007) both modified a log-linear model which included stochastic effects that satisfy a Wiener process to describe the degradation path of fluorescent lamp and the light intensity in light-emitting diode, respectively. Peng and Tseng (2009) present a generalized linear degradation model for lasers in which unit-to-unit variations, the stochastic measurement-to-measurement errors. The Arrhenius life-stress model is a traditionally used tool for temperature dependent life tests, for example, Kim et al. (2013) used different temperature conditions as the accelerated factor and the Arrhenius model to describe the moisture-induced degradation of the multi-crystalline silicon solar cells. Ott et al. (2013) used different temperature conditions as the accelerated factor to obtain mean times to failure of CIGS solar cells and fitted the results using an Arrhenius model.

Up to the present date, extensive efforts have been focused on the improvement of stability of DSSCs by changing the electrolytes. However, little has been found in the literature on prediction of the efficiency in DSSCs under ambient conditions, i.e. estimation shelf-life has not been discussed. In this work, we report results of accelerated degradation tests on three types of DSSC: one using a volatile organic solvent 3-methoxy-propionitrile (MPN), one using a nonvolatile organic solvent polyethylene-glycol-di methyl-ether (PEGDME), and one using an ionic liquid 1-ethyl-3-methyl-imidazolium tetra-cyanoborate (EMITCB). The results were analyzed using the degradation model proposed by Peng and Tseng (2009), which was available in the package iDEMO (Cheng and Peng, 2012) written in R. Shelf-life predictions were carried using the model.

## 2. Experiment

### 2.1. Chemicals

FTO glass (13 Ω/□, Nippon Sheet Glass), $TiO_2$ (20 nm in size) are purchased from Eternal Chemical Co., Ltd, N719 (Everlight Chemical Industrial Co., Ltd). Surlyn (30 um thickness, Solaronix), Lithium iodide (LiI, 99.9%), Polyethylene glycol dimethyl ether (PEGDME, MW ~ 250), tetrabutylammonium iodide (TBAI, 98%), 4-tert-butylpryridine (TBP, 99%), iodine ($I_2$, 99.5%) are purchased from Sigma–Aldrich. Ammonium iodide ($NH_4I$, 99%), N-methylbenzimidazole (NMB, 99%), 3-Methoxypropionitrile (MPN, 99%) are purchased from Alfa Aesar. Guanidine Thiocyanate (GuSCN, $\geqslant$99%), 1-Ethyl-3-methylimidazolium tetracyanoborate (EMITCB), 1-methyl-3-propylimidazolium iodide (PMII) are purchased from Merck.

### 2.2. Preparation of DSSCs

The anode was prepared by screen-printed double-layer $TiO_2$ with a total thickness of 14 μm (10 μm nano-$TiO_2$